

ROLE OF OXYGEN IN ALKALI-CATALYZED HYDROGEN GASIFICATION OF CARBON BLACK

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INTRODUCTION

The hydrogen gasification of carbon in the presence of alkali metal salts has been reported in only a few studies [1-3], and little information about reaction kinetics or catalytic enhancement is available. The uncatalyzed reaction, in contrast, has received considerable attention [4,5]. Of particular interest are the results of Cao and Back [6] and Blackwood [7], who reported the effects of oxygen on the methane production rate.

Hydrogen gasification is under investigation in our laboratory because it is a direct route to methane production and because it offers a unique environment in which to study gasification catalyst behavior. Hydrogen gasification involves an elemental feed gas (H_2) and a single product (CH_4), thus facilitating accounting of carbon and oxygen from both reactant and catalyst during gasification. The work presented in this paper focuses on the importance of oxygen in hydrogen gasification, and discusses results of experiments involving both alkali-metal catalyzed and uncatalyzed reactions. This study is a continuation of earlier work [8].

EXPERIMENTS

The carbon used in this study is a graphitic carbon lampblack (Fisher Scientific) with an initial BET surface area of 20 square meters per gram and an impurity content of less than 0.1 per cent. The catalysts (K_2CO_3 , Na_2CO_3 , KCl) were deposited on the carbon by wet impregnation in metal to carbon molar ratios of approximately 0.01 and 0.02. Uncatalyzed carbon samples were also put through the same impregnation procedure but without addition of catalyst. Actual M/C ratios, measured by neutron activation analysis, are $K/C = 0.0093$ and 0.0192 for K_2CO_3 , $Na/C = 0.0111$ and 0.0221 for Na_2CO_3 , and $K/C = 0.019$ for KCl. Typical sample sizes gasified were 60-70 milligrams.

The gasification apparatus consists of a fixed bed differential reactor equipped with a gas collection system and gas chromatograph for rate measurement and product gas analysis. The pressure vessel is a Haynes Alloy tube (0.875" ID and 2.0" OD) designed for simultaneous operation at 1000°C and 1000 psi. Rate is measured as rate of methane evolution via timed collection of product gas; evolution rates as low as 0.005 ml/min can be accurately measured. Further details are given elsewhere [8].

All gasification experiments were carried out in pure hydrogen (Airco, 99.999%) at 500 psi pressure and a flow rate of 3-5 liters(STP)/minute/gram initial carbon. In all reactions the apparatus was evacuated three times and then purged in helium during initial heating. Hydrogen was then added to the reactor at 500°C in most experiments. In some experiments uncatalyzed samples were degassed by heating to 1000°C in vacuum for twelve hours before gasification, and in others hydrogen was added at room temperature.

RESULTS

All gasification experiments were conducted in a large excess of hydrogen, so that the methane formation reaction was far from equilibrium. In addition, repeated experiments in which sample size and flow rate were changed and in which sample temperature was measured allow us to conclude that the results represent intrinsic and reproducible kinetic rate measurements for the hydrogen gasification.

Catalyzed Gasification: The experimental data are represented as rate of methane evolution versus time during gasification. The start of reaction ($t=0$) is taken as the time where hydrogen is added to the reaction vessel (500°C); steady state temperature is reached after about 55 minutes. In the Figures, the symbols represent individual collection points; the curve represents the best fit of the rate data. Methane evolution rate is normalized to initial carbon weight; integration of the rate curve gives a carbon conversion close to that obtained by weighing the sample residue.

Methane evolution rate for gasification in the presence of Na_2CO_3 and K_2CO_3 catalysts at 865°C are given in Figure 1 for $\text{M/C} = 0.02$ and in Figure 2 for $\text{M/C} = 0.01$. The rate curve for sodium is scaled to the same M/C ratio as potassium. The results show that both catalysts enhance the rate of hydrogen gasification, but show different catalytic effects as carbon is consumed. For Na_2CO_3 , rate is a maximum near the time where steady state temperature is first reached, whereas for K_2CO_3 the rate increases as gasification proceeds. The results for gasification in the presence of KCl are also given in Figure 1, and show that KCl has little catalytic effect in hydrogen gasification.

Activation energy of the hydrogen gasification reaction was measured over the temperature range of 780 – 900°C for the uncatalyzed reaction and in the presence of the carbonate catalysts. The Arrhenius plots are given in Figure 3 at 20% carbon conversion for all three samples; also shown (by dotted line) is the plot at 30% conversion for the Na_2CO_3 sample. The calculated activation energy at 20% conversion is 220 kJ/mole for K_2CO_3 , 251 kJ/mole for Na_2CO_3 , and 264 kJ/mole for the uncatalyzed reaction. The lower value for the potassium catalyst results from scatter in the data, as potassium catalyst gave the highest reaction rate and thus the fewest number of collection points. Therefore, the activation energy is the same within experimental uncertainty for both catalyzed and uncatalyzed reactions and approximately equal to 250 kJ/mole.

The different gasification rate curves for sodium and potassium catalyzed reactions led to investigation of the interaction between catalyst and carbon and evolution of oxygen species during heatup. In these experiments, the reactor was purged as usual, but the sample was heated in hydrogen and gas evolution was monitored during heatup. The results of these experiments are given in Table 1. The primary gas evolved from K_2CO_3 is CO_2 , which appears in the temperature range of 300 – 500°C , while Na_2CO_3 releases primarily CO at 400 – 700°C . The uncatalyzed reaction releases very small quantities of each gas at similar temperatures, probably from weakly bound oxygen species on the carbon surface.

TABLE 1
Gas Evolution during Sample Heatup
(M/C = 0.02)

Catalyst	CO (mg)	CO ₂ (mg)	Total Oxygen (mg)	Fraction of Oxygen in Catalyst Evolved	
				as CO	as CO ₂
K ₂ CO ₃	0.50	1.05	1.04	0.12	0.31
Na ₂ CO ₃	1.05	0.29	0.81	0.22	0.05
none	0.031	0.102	0.093	-	-

Uncatalyzed Gasification: The effects of indigenous oxygen, present on the surface or in the bulk of the unimpregnated carbon, was investigated by conducting several experiments in which the carbon was either degassed or partially reacted in oxygen. Carbon was degassed by heating to 1000°C in vacuum to remove adsorbed oxygen. Oxygen was replenished on the carbon surface by partial combustion in air at 400°C. The partial combustion was controlled by admitting a finite amount of oxygen into the pressure vessel and then allowing the reaction to go to completion.

Results of the experiments are given in Figure 4 as methane formation rate versus carbon conversion. The solid circles represent rate for an untreated sample. The open squares represent a sample initially degassed, gasified in hydrogen (to 20% conversion), partially combusted in oxygen (to 35% conversion), and then further gasified in hydrogen. The open triangles represent a sample initially gasified in hydrogen (to 25% conversion), partially combusted in oxygen (to 35% conversion), and then further gasified in hydrogen. The results show that degassing reduces gasification rate, and that partial combustion in oxygen recovers some reactivity toward hydrogen. It was necessary to partially combust the carbon to recover reactivity; an experiment in which the carbon was exposed to oxygen at room temperature showed no subsequent increase in reactivity toward hydrogen, thus indicating little reaction between oxygen and carbon.

DISCUSSION

Figures 1 and 2 illustrate that both sodium and potassium carbonate are effective hydrogen gasification catalysts. The curves also show that the gasification rate changes significantly as carbon is consumed, and in a different manner for each catalyst.

Two quantities pertaining to gasification of this carbon, measured in an earlier work [8], must be mentioned. First, specific BET surface area of the carbon black increases dramatically during gasification [8], increasing approximately linearly with conversion from 20 m²/g initially to 400 m²/g at sixty per cent conversion for both catalyzed and uncatalyzed reactions. Absolute carbon surface area therefore increases about six-fold up to 60% conversion. Specific reaction rate based on this area is nearly constant for the K₂CO₃-catalyzed samples over the course of gasification, but decreases strongly for other samples. This indicates that, at least for the uncatalyzed case, rate is not related to total surface area. Secondly, significant catalyst is lost from the sample during gasification [8]; the amount of catalyst after gasification, determined by neutron activation analysis, decreases linearly with conversion to approximately one-third of

the initial value at 80% for both Na_2CO_3 and K_2CO_3 . Total surface area development and catalyst loss do not explain the increase in rate with conversion, however, and other factors must therefore account for the observed behavior.

The Arrhenius plot in Figure 3 shows that apparent activation energy is nearly the same both for catalyzed and uncatalyzed reactions and at different conversions. This is in accordance with results of other investigators [9-10] for steam and carbon dioxide gasification, and suggests that the role of the catalyst is to increase the number of active sites without changing the reaction mechanism. This indicates that the active sites in both catalyzed and uncatalyzed gasification must perform a similar function, and that different shapes of the rate curves in Figures 1 and 2 for sodium and potassium catalysts must be attributed not to different reaction mechanisms but to differences in active site population as gasification progresses. The value of apparent activation energy (250 kJ/mole) is somewhat higher than values reported (150-210 kJ/mole) [4,5,11] for uncatalyzed methane formation. The only study for which a higher activation energy (300 kJ/mole) was found was for the reaction with graphite at 1200-1600°C [12]. This is further evidence that the rate measurements represents intrinsic reaction kinetics, and suggests that values of activation energy measured for porous carbons and chars may include effects of diffusion resistances and mineral matter.

Results from degassing and partial combustion of uncatalyzed carbon, given in Figure 4, show that the presence of oxygen on the carbon surface strongly enhances gasification rate. This is in agreement with the results of Cao and Back [6], who report an order of magnitude increase in methane formation rate when 0.1% oxygen is added to the hydrogen feed stream, and with the results of Blackwood [7], who observed that methane formation rate was proportional to oxygen content of coconut char. If oxygen is the key entity which enhances gasification rate, then the observed decrease in rate with time for uncatalyzed and untreated carbon (solid circles in Figure 4) is consistent with the concept that surface oxygen is slowly stripped from the carbon during reaction at 865°C. This concept is supported by the slower or nearly nonexistent decrease in rate with time for the uncatalyzed reaction at lower temperatures, in which oxygen is not removed from the surface.

Degassing the carbon (open squares in Figure 4) decreases the rate to a low level (0.8 ml $\text{CH}_4/\text{min}/\text{gram C}$) which is essentially invariant with time. The finite rate after degassing results either from the intrinsic carbon-hydrogen reactivity or from the presence of low levels of oxygen impurities in the carbon or reactant gas. When the degassed sample is combusted in oxygen at 400°C, gasification rate increases by approximately 2.0 ml $\text{CH}_4/\text{min}/\text{gram C}$. Similarly, when a sample not initially degassed (triangles in Figure 4) is combusted in oxygen at 400°C the rate also increases by approximately 2.0 ml $\text{CH}_4/\text{min}/\text{gram C}$, suggesting that partial combustion results in formation of a similar number of new active sites in both cases. Further, these results indicate that new active sites are formed in addition to those already existing on the surface. The total methane evolution rate is therefore the sum of the rates from the original oxygen-bearing sites which are still active and from the sites created by partial combustion.

The different rate curves for sodium and potassium carbonate catalysts and the evolution of different gases during heatup shows that the catalyst-carbon interactions are substantially different for the two cases. For K_2CO_3 ($\text{M/C}=0.02$), the evolution of one-third of the oxygen in the catalyst as CO_2 is consistent with results reported by Mims and Pabst [13] and Wood and Sancier [14] for formation of a surface oxide. It is not known at this time

if a K-O-C type complex is formed in the presence of hydrogen; however, based on the fact that absolute rate increases and specific rate is maintained, it can be concluded that the potassium catalyst disperses in a stable state on the carbon surface and forms new active sites as gasification progresses. These observations are consistent with those reported for a surface oxide complex; however no conclusions can be made.

The low initial catalytic activity for K/C=0.01 samples and the observed pyrophoric nature of potassium-containing sample residues from low temperature gasification make it impossible to rule out intercalation of potassium as an intermediate step in gasification. This phenomena has been dismissed for carbon oxidation reactions but has not been investigated for the reducing hydrogen gasification environment, and it is possible that both intercalation and surface oxide formation take place. Intercalation is reported to be a sink for potassium [15], thus explaining the low initial activity for K/C=0.01 samples. Sodium does not intercalate; this may provide an explanation of observed gasification behavior.

For the Na_2CO_3 catalyst, evolution of primarily CO at higher temperatures during heatup suggests that the carbothermic reaction is taking place. It has been reported that sodium metal interacts with surface oxygen [16] to form an oxide complex similar to that for potassium; it is possible that such a complex is responsible for the catalytic activity.

Two observations suggest that the interaction of the sodium catalyst with carbon is not as strong as that of potassium. First, after gasification in hydrogen the carbon residues contained visible particles of sodium carbonate, indicating that significant agglomeration of catalyst occurred. Also, the total amount of oxygen evolved during heatup for the M/C=0.02 samples (Table 1) was less for sodium than for potassium. These observations indicate that the overall interaction of sodium carbonate with carbon is not as strong as the interaction of potassium carbonate with carbon, and it is likely that sodium forms few new active sites as gasification proceeds. The observed rate is therefore seen to decrease with conversion.

The mechanism by which the oxygen-bearing species (whether oxygen in the uncatalyzed sample or an M-O- complex for the catalyzed reactions) promote hydrogen gasification has not been studied. However, there is some evidence which allows the role of these species to be postulated. Yang and Duan [17] have recently reported using etch pit analysis that the arm-chair {1121} face of graphite is more reactive than the zig-zag {1011} face, and that hydrogen inhibits gasification in CO_2 and H_2O by preferentially adsorbing on and thus stabilizing the zig-zag face. The presence of hydrogen results in the formation of hexagonal (zig-zag) etch pits of low reactivity. Along with this, chemisorbed hydrogen is known to strongly bind to carbon and reduce oxygen adsorption capacity [18]. In contrast, gasification in CO_2 alone results in round pits with arm-chair edges. For hydrogen gasification, Zielke and Gorin [11] postulated that reaction is sterically more suited to the arm-chair face. Thus it is likely that the function of the oxygen-bearing surface species is to maintain and propagate arm-chair reaction sites on the carbon during gasification. Removal of oxygen species, either by desorption or reduction, results in consumption of arm-chair sites, leaving only residual and unreactive zig-zag faces to which hydrogen strongly binds. Combustion in oxygen results in formation of new arm-chair faces, resulting in enhancement of hydrogen gasification rate. Similarly, the addition of catalyst results in the presence of a larger quantity and possibly more stable oxygen-containing species which propagate the arm-chair faces, thus catalyzing the reaction.

This idea is also consistent with results reported by Baker et al., [19] and Tomita and Tamai [20] for barium and transition metal catalyzed hydrogen gasification, in which reaction occurs via channeling of catalyst particles in the $\langle 1120 \rangle$ crystallographic direction. The residual zig-zag faces left by the channel show no reactivity. These catalysts therefore propagate the arm chair face at the head of the channel, resulting in continued gasification.

CONCLUSIONS

The similar apparent activation energy and surface area development for uncatalyzed and catalyzed hydrogen gasification reactions suggests that catalysts increase the number of available reaction sites without changing the reaction mechanism. Surface oxygen enhances the rate of gasification; this along with evolution of CO_2 from potassium carbonate during heatup makes possible the idea that a surface oxygen complex is the catalytic agent. Based on evidence in the literature, the role of surface oxygen is postulated to be propagation of the arm-chair configuration of edge sites during gasification. These arm-chair sites are believed to be the sites at which hydrogen gasification occurs.

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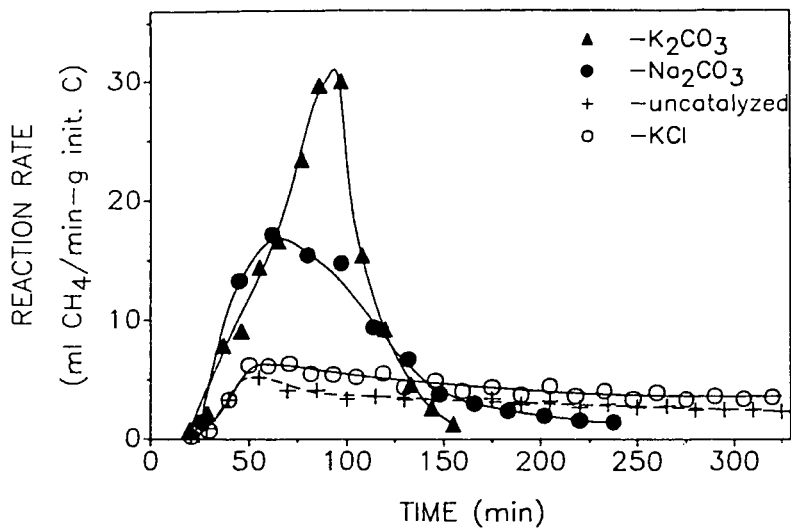


FIGURE 1. Methane evolution rate at 865°C for M/C=0.02

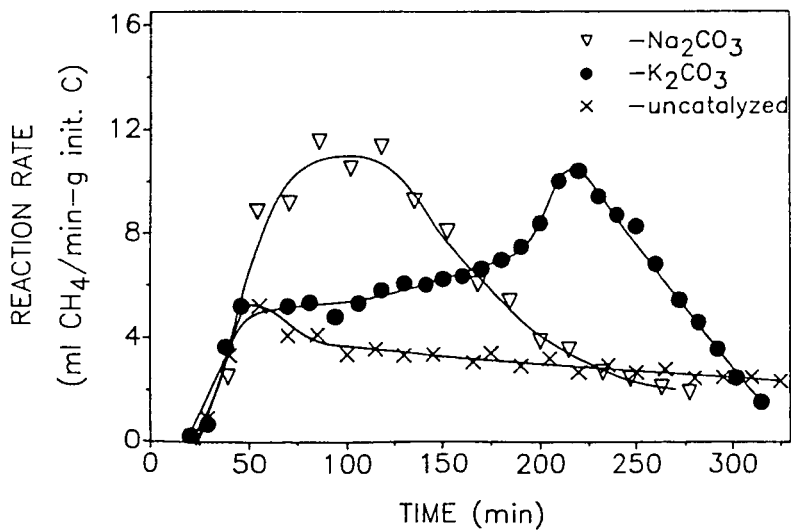


FIGURE 2. Methane evolution rate at 865°C FOR M/C=0.01

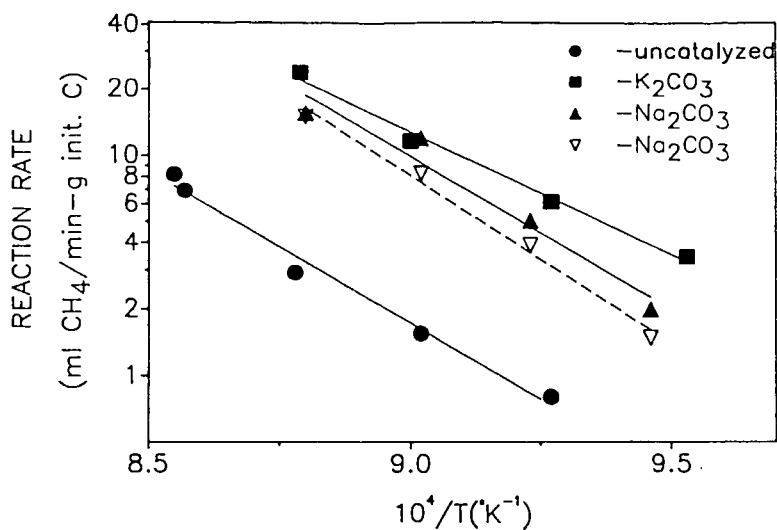


FIGURE 3. Arrhenius plot for $M/C=0.02$

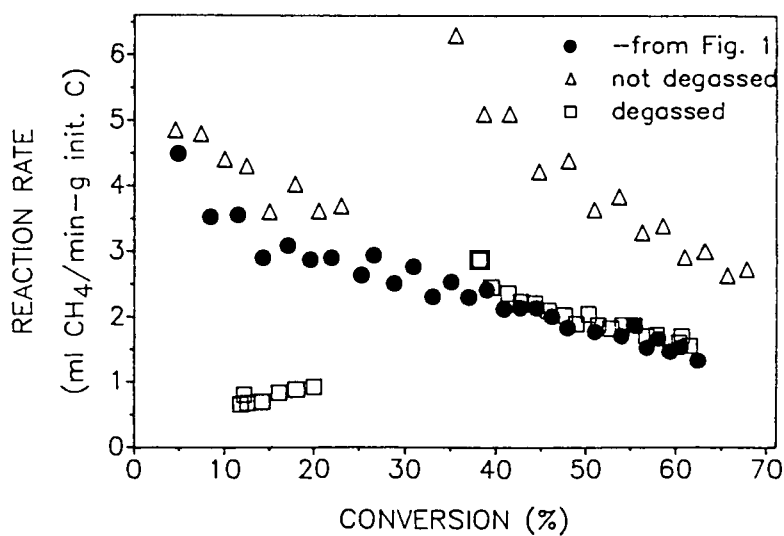


FIGURE 4. Oxygen effects on uncatalyzed rates.